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ZINCIAN CHROMITE FROM OUTOKUMPU, FINLAND[1]

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ABSTRACT

Chromite from the Outokumpu Mine in Finland as described by Vahätälo (1953) has an anomalous composition, ostensibly with RO:R_2O_3 ratio of 0.80 or less. Re-examination by the authors shows that the original analysis apparently overlooked 5.8 per cent ZnO in the chromite; counting this as RO brings the ratio to a more satisfactory 0.96. This zinc content is the highest by far for any chromite reported. Chemical and spectrographic analyses, and x-ray powder data are presented; the cell constant is $\alpha = 8.345$ Å.

The presence of eskolaite, with abundance of chromium-bearing silicates, and the corrosion of the chromite are believed to be more consistent with hydrothermal alteration of relict chromite stringers in place, than with hydrothermal emplacement of chromite in "dikes" at Outokumpu.

GENERAL INFORMATION

In his monograph on the geology of the Outokumpu ore deposits in Finland, V. O. Vahätälo (1953, p. 39) describes

> "Some chromite dikes cutting . . . diopside skarn in the mine in the Kaasila area . . . , about 2 m in thickness, . . . situated below the footwall of the ore at the contact-zone of quartzite and serpentine . . . there is a network of thin, irregular intercrossing chromite dikes. The thickness of the dikes varies from 1 mm to 15 mm."

Because the chromite is of unusual composition, is in an unusual environment, and the analysis (A, Table I) presents some questions, another sample of chromite, presumably from the same "dikes," was obtained from the Mineralogisches Institute, Heidelberg, through the kindness of Professor Paul Ramdohr.

The specimen was a few centimeters across and contained a chromite band a few millimeters wide. The band, although superficially homogeneous, actually is rather complex. The chromite grains are translucent red and show irregular light and dark zones. Bright green weakly anisotropic uvarovite borders the chromite band and cuts across it. Chrome-diopside forms most of the gangue, with minor carbonate (calcite), some small rounded sphene (?) with black opaque nuclei, and small irregular masses of pyrrhotite with a very little chalcopyrite.

The "dike material" analyzed by von Knorring (Vahätälo, 1953, p. 39) is described as "almost exclusively of chromite, in addition to which some uvarovite and diopside as well as occasional quartz grains are met with."

Zinc is now known to be present in chromite from three localities: in

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[1] Publication authorized by the Director, U. S. Geological Survey.

Finland,[1] Ramberget, Norway (Donath, 1931) (C, Table I), and, in much smaller quantity, from the Woods mine, Maryland (Pearre and Heyl, 1960). Cleaned chromite from the Woods Mine gave by spectrographic analysis 0.5 per cent Zn, with 0.3 per cent each of Mn and Ni, and 0.2 per cent Ti; *x*-ray fluorescence study by Harry Rose, Jr., confirmed the presence of zinc in this chromite ore, and optical examination of a thin section showed no sphalerite.

Table I. Analyses of Zincian Chromite from Outokumpu Mine Finland, and Ramberget, Norway

	A	B	C
SiO_2	4.90	2.8	1.74
Al_2O_3	8.20	7.4	.35
Cr_2O_3	57.10	54.0	41.48
Fe_2O_3	—	3.0	50.49
FeO	22.20	17.1	—
MnO	3.30	2.0	—
MgO	2.56	4.3	4.68
CaO	0.20	.54	—
TiO_2	—	< 0.1	—
H_2O	0.44	1.55 ($H_2O+0.25$)	—
ZnO	—	5.8	2.62
Mo	0.32 “as	—	—
S	0.30 molybdenite”	—	—
	99.52	98.6	100.36
Cr/Fe	2.3	2.4	0.80
Approximate norms of chromite (see text)			
RCr_2O_4[1]	—	82.5	64.2
RAl_2O_4	—	16.7	0.8
RFe_2O_4	—	0.9	35.1
MgO/RO	—	13.5	15.3

A. “Chromite dike” Outokumpu, O. v. Knorring, analyst. All Fe as FeO (Vahätälo, 1953, p. 39).

B. “Chromite dike” Outokumpu, J. I. Dinnin and Harry Rose, Jr., U. S. Geological Survey, analysts.

C. Chromite from Ramberget, Norway, M. Donath, analyst. All Fe as Fe_2O_3 (Donath, 1931, p. 484).

[1] R includes Mg, Fe^{2+}, Mn^{2+}, Zn.

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[1] After our sample had been analyzed, we learned from Dr. Kouvo (personal communication, 1963) that Finnish geologists have known about the zinc for some time.

COMMENTS ON ANALYTICAL PROCEDURES

The results of the U. S. Geological Survey analyses (Tables I and II) differ from von Knorring's mainly in the presence of 5.8 per cent ZnO. The sample analyzed was coarsely crushed, and optically homogeneous grains were hand-picked. Very little, if any, silicate mineral was observed, although the analysis showed 2.8 per cent SiO_2. In view of the sulfides accompanying the chromite, it seemed possible that deep red sphalerite might be present and be mistaken for chromite. To check this possibility chromite grains were examined in polished section with electron microprobe; individual grains (30–50μ in diameter) were found to contain major chromium, iron, and zinc but no sulfur, showing that the bulk, at least, of the zinc is in the chromite.

TABLE II. SPECTROGRAPHIC ANALYSIS OF CHROMITE FROM OUTOKUMPU
Helen W. Worthing, U. S. Geological Survey, analyst

Si	1.5	Ti	.03	Mo	.005	Zr	.0005
Al	3.	Mn	1.5	Ni	.05		
Fe	Major	Ag	.002	Sr	.0005		
Mg	2.	Co	.02	V	.02		
Ca	.15	Cr	Major	Y	.001		
Na[1]		Cu	.00003	Yb	.0001		
Ba[1]		Ga	.003	Zn	>2.6		

Looked for but not detected: K, P, As, Au, Be, Bi, Cd, Ce, Ge, Hf, Hg, In, La, Li, Nb, Pb, Pd, Pt, Re, Sb, Sc, Sn, Ta, Te, Th, Tl, U, W.

[1] A large amount of chromium interferes with the detection of small amounts of sodium and barium.

Results are reported in weight per cent to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15 and 0.1, etc., which represent approximate midpoints of group data on a geometric scale. The assigned group for semiquantitative results will include the quantitative value about 30% of the time.

An *x*-ray powder pattern of the chromite (Table 3) showed no sensible difference from other ordinary chromites because of the zinc, as might be expected from comparison of the several mol. ratios of the divalent atoms, calculated from analysis B in Table I, with their corresponding ionic ratios in octahedral coordination.

	Mol. Ratio	*Ionic Radius*
Fe^{2+}	58.5	0.83
Zn^{2+}	17.4	0.83
Mg^{2+}	17.2	0.78
Mn^{2+}	6.9	0.91

If the zinc is regarded as replacing ferrous iron, the lattice constant would be essentially unchanged, and if magnesium, the change should be small.

Composition of the Chromites

The composition of the chromite from Outokumpu cannot be calculated with certainty because of inconsistencies between the analyses and the recognized gangue minerals. The U. S. Geological Survey analysis shows only about one-fourth of the CaO needed to account for all the SiO_2 as diopside or a fifth of the CaO needed for uvarovite, according to Vahätälo's data (1953, p. 38) on these minerals; the balance of SiO_2 remaining after diopside was therefore calculated as serpentine, the most likely other gangue mineral. Von Knorring's analysis shows only 5 per cent of the CaO need to account for the SiO_2 as uvarovite, and not enough CaO and MgO together to account for the SiO_2 as diopside, but he described some quartz in his sample. Donath reported olivine as the impurity in the Ramberget sample, and it presents no difficulty.

Table III. *X*-ray Powder Data, Chromite, Outokumpu, Finland
Cu radiation, Ni filter, camera diameter 114.6 cm

I	d Å	hkl	α_0
w	4.822	111	8.352
s	2.947	220	8.335
vvs	2.515	311	8.341
vw	2.404	222	8.322
s	2.092	400	8.367
w	1.702	422	8.338
vs	1.605	511 or 333	8.340
vs	1.475	440	8.345
vw	1.3195	620	8.345
w	1.274	533	8.354
vw	1.259	622	8.351
vw	1.205	444	8.349
		Mean	8.345 Å
		Standard error of mean	0.097

The ratio $RO:R_2O_3$, an important factor in chromite composition, has been determined by analyzing for both FeO and Fe_2O_3 only in the Geological Survey analysis; after calculation of the SiO_2 as diopside and serpentine, the indicated ratio is 0.9:1; and omitting SiO_2, CaO and H_2O, the $RO:R_2O_3$ ratio is very close to 1:1. Von Knorring's analysis cannot be calculated to a 1:1 $RO:R_2O_3$ ratio even with all the Fe as FeO, and none of the other RO constituents deducted as silicate. For comparison on a normative basis, the Geological Survey and Ramberget analyses were calculated to 1:1 ratios after deduction of silicate impurity.

Compared to unaltered podiform chromite in alpine peridotites (Stevens, 1944; Thayer, 1946) the chromite from Outokumpu is abnormally rich not only in zinc, but in manganese as well; furthermore, it is abnormally low in magnesium. The Ramberget material contains an abnormal amount of zinc, is low in magnesium, and almost lacking in aluminum. The average podiform-type chromite contains 0.1–0.3 weight per cent MnO, and on a normative basis (Thayer, 1956, p. 28) falls within the following ranges (in mol. per cent): $(Mg, Fe)Cr_2O_4$, 18–81; $(Mg, Fe)Al_2O_4$, 17–81; $(Mg, Fe)Fe_2O_4$, 0.6–10. The ratio of MgO:total RO ranges between about 50 and 75 mol. per cent. It appears, therefore, that occurrence of zinc in chromite is associated with deficiency in MgO and other anomalies in composition, such as low Al_2O_3 and unusually high iron oxide or MnO.

ORIGIN OF THE CHROMITE AT OUTOKUMPU

The occurrence of chromite in dolomite and skarn rocks as well as serpentinized peridotite at Outokumpu has led to differing opinions on its origin. Although Haapala (1936, p. 75) believes that all the chromite was early magmatic, Vahätälo (1953, p. 40) and Kouvo and Vuorelainen (1958, p. 1099) believe that it was hydrothermally introduced. Thayer has argued (1956, p. 40) that the chromian spinels crystallized in equilibrium with olivine and pyroxene in magnesium-rich environments are unstable under hydrothermal conditions; conversely, any chromian spinels formed hydrothermally should have very different compositions. The occurrence of eskolaite, Cr_2O_3 (Kouvo and Vuorelainen, 1958), abundance of chromium-bearing silicates, and corrosion of chromite described by Vahätälo (p. 39), all indicate conditions of disequilibrium with primary chromian spinel. The abnormal composition of the chromite itself is consistent with the environment, but there is no evidence that it was in equilibrium with the sulfide-bearing solutions. Hydrothermal alteration of chromite generally is marked by great increase in Fe^{3+} (Amin, 1948, p. 133; Miller, 1953, p. 1146); the presence of sulfides at Outokumpu, however, indicates an unusually low redox potential.

The occurrence of the chromite "dikes" as described by Vahätälo (p. 32), in a two-meter skarn zone between peridotite and quartzite, could be explained by silication of peridotite or serpentine containing stringers of magmatic chromite. Stringers of chromite that unquestionably were formed in fresh dunite by magmatic flowage (Thayer, 1956, Fig. 2.7) may closely resemble true veins, especially after metamorphism like that at

Outokumpu. Although the evidence for local migration of chromium is indisputable, we believe that all the chromite at Outokumpu can be explained as relict, either as a primary mineral in peridotite, or as detrital grains in the sedimentary rocks.

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